^{107}Ag and ^{109}Ag Nuclear Magnetic Resonance Studies of Ag$^+$ Ions in Aqueous Solutions

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The NMR lines of ^{107}Ag and ^{109}Ag have been investigated in aqueous solutions of AgF, $AgNO_3$, and $AgClO_4$. The ratio of the Larmor frequencies of ^{109}Ag and ^{107}Ag has been measured in various samples: $\nu(^{109}\text{Ag})/\nu(^{107}\text{Ag}) = 1.149\,639\,7\,(8)$. No primary isotopic effect was to be detected within these limits of error (0.7 ppm). This ratio yields the hyperfine structure anomaly $^{107}\Delta^{109} = -0.004\,127\,7\,(7)$. The concentration dependence of the chemical shift of the ^{107}Ag and ^{109}Ag resonance frequencies was determined. Using this dependence, the ratios of the Larmor frequencies of the ^{107}Ag and ^{109}Ag nuclei for infinite dilution relative to the resonance frequency of ^{73}Ge in $GeCl_4$ are given. The magnetic moments of the ^{107}Ag$^+$ and ^{109}Ag$^+$ ions merely surrounded by water molecules are $\mu(^{107}\text{Ag}^+) = -0.113\,045\,3\,(9)\,\mu_N$ and $\mu(^{109}\text{Ag}^+) = -0.129\,961\,5\,(10)\,\mu_N$ without diamagnetic corrections. These values are compared with the result of an atomic beam experiment, the difference of the moments is due to the shielding of the silver nuclei by water molecules around the ions. The shielding constant is σ^* (Ag$^+$ in H_2O vs. Ag atom) $= -0.000\,94\,(17)$. Preliminary values of the relaxation times are given.

1. Introduction

The isotopes ^{107}Ag and ^{109}Ag have both the nuclear spin $I = 1/2$ [1]. In our magnetic field of 1.807 Tesla, their Larmor frequencies are $\nu(^{107}\text{Ag}) = 3.114$ MHz and $\nu(^{109}\text{Ag}) = 3.579$ MHz. The abundances of these silver isotopes are 51% and 49% respectively.

The NMR signals of ^{107}Ag and ^{109}Ag in a 1 molar solution of an Ag salt, are about 7 orders of magnitude weaker than the proton NMR signal in water in the same magnetic field B_0, and with the same probe volume.

There are only two ^{107}Ag and ^{109}Ag measurements [2, 3]. Both authors have used aqueous $AgNO_3$ solutions as samples with 7 molar and 6 molar concentrations respectively. In both experiments the samples were doped with paramagnetic ions to reduce the relaxation times T_1 and T_2, i.e. to broaden the extremely weak NMR lines beyond the line width caused by the inhomogeneity of the field B_0; the samples were 1 molar and 2 molar in $Mn(NO_3)_2$ respectively. Such admixtures can cause considerable shifts of the NMR lines [4], which is undesired in most cases.

The reason for the few measurements, is probably the weak NMR signal of both silver isotopes, and also the long relaxation times, which require paramagnetic admixtures using any conventional measuring technique. The present investigations were performed with the Quadriga-technique [5], which avoids any paramagnetic admixtures.

2. Experimental

2.1 Apparatus

The apparatus, developed to detect very weak NMR signals, is a pulse spectrometer, described in [6, 7]. The magnetic field $B_0 = 1.807$ Tesla is stabilized with a ^{7}Li-NMR probe [8]. The spatial homogeneity of the field ($|\Delta B_0| \leq 5 \cdot 10^{-6}$ Tesla in the range of the relatively large NMR sample) is achieved by special nickel-shims. The temperature of the samples was held constant within a range of ± 1 K by a thermostat. The NMR signal between the rf-pulses, was accumulated in a time averaging computer (Signal analyzer 5480 A of Hewlett-Packard), to improve the signal/noise-ratio.

2.2 Measuring Technique and Evaluation of the NMR Signals

All measurements of ratios of Larmor frequencies and also of chemical shifts were performed with the Quadriga Fourier Transform technique [5]. This is a steady-state free precession technique with periodical irradiation of equal rf-pulses, especially developed for slowly relaxing systems, i.e. systems with relaxation times T_1, $T_2 \gg T_2^*$ (T_2^* is the time constant for the decay of the NMR signal due to the inhomogeneity of the field B_0).

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If the condition $T \ll T_2^*$ is fulfilled by choosing a sufficiently small pulse period T, then maximum NMR signal can be achieved, i. e. any loss of NMR signal due to the inhomogeneity of the field B_0 can be avoided. Shifts between the maximum of the NMR line, resulting from such a steady-state, and the Larmor frequency, are cancelled by performing four measurements with systematically varied frequencies of the rf-field, during the pulses. By this technique admixture of paramagnetic impurities with its well known disadvantages can be avoided.

The signal stored in the time averaging computer, is transferred by punched tape to a computer (CDC 3300 of the Zentrum für Datenverarbeitung, Tübingen) to calculate the Quadriga Fourier Transform. The shape of the NMR line obtained by this transformation is given by

$$I(\nu) = \sin 2\pi T(\nu_L - \nu)/2\pi T(\nu_L - \nu) ,$$

ν_L is the Larmor frequency. The halfwidth of this NMR line is $\Delta\nu_{1/2} = 0.6/T$, which is independent of the natural width of the NMR line. This less familiar line shape, is the price to be paid for the advantages mentioned above.

For all measurements, a pulse repetition rate of 45 Hz was chosen, i. e. the pulse period was $T = 22.2$ msec $\approx T_2^*/2.5$. This is a reasonable compromise between maximum signal amplitude and narrow NMR line. Figure 1 shows the NMR line of the ^{107}Ag resonance of the reference sample No. 4 (see Sect. 3.1); within a total measuring time of 12 minutes (4×3 min) a signal/noise-ratio of more than 100 was to be achieved.

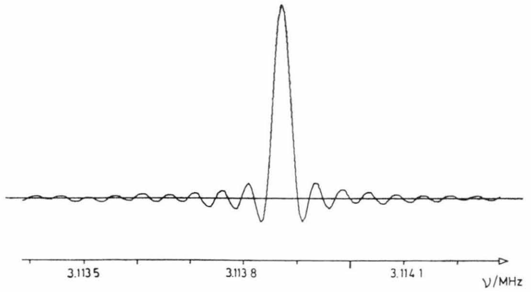

Fig. 1. ^{107}Ag NMR signal of reference sample No. 4 in a spherical sample of 17 mm internal diameter. Measuring time 12 minutes (4×3 min).

To determine chemical shifts as well as ratios of Larmor frequencies the sample replacement technique was used.

As the silver nuclei ^{107}Ag and ^{109}Ag have small magnetic moments and no quadrupole moments, very long relaxation times are to be expected. The measurement of such long relaxation times, with spin-echo techniques would require enormous measuring times, as the experiment must be repeated frequently to achieve a sufficient signal/noise-ratio, and before each experiment the installation of the thermal equilibrium of the system must be waited for, which requires about $5 \cdot T_1$. To overcome these difficulties a new technique[9] was developed to measure such long relaxation times of nuclei with very weak NMR signals; this is a steady-state technique, which avoids any waiting time for the thermal equilibrium.

2.3 Samples

For the measurement of chemical shifts, the following samples were used: The $AgNO_3$ and $AgClO_4$ solutions were contained in glass cylinders of 21 mm internal diameter. For the AgF solutions polypropylene cylinders of 21 mm internal diameter had to be used. To measure the ratios of the Larmor frequencies of ^{107}Ag and ^{73}Ge and also of ^{109}Ag and ^{73}Ge, spheres of 17 mm internal diameter were used as well as cylinders of 21 mm internal diameter.

The Ag salts $AgClO_4$ and AgF were delivered by Alfa Inorganic, Inc., Beverly (No. 22125 respectively No. 10125) with a purity of 97 . . . 99%, whereas $AgNO_3$ was manufactured by E. Merck AG, Darmstadt (No. 1512), which was analytical grade. The water used as solvent had a conductivity of $10^{-6}\ \Omega^{-1}\ \text{cm}^{-1}$.

Preparing the AgF solutions, always some metallic Ag dropped out, which had to be filtered. The concentrations of these solutions were determined from their densities by using the values of Jahn-Held and Jellinek[10]. The concentrations of the $AgNO_3$ and $AgClO_4$ solutions were determined by weighing Ag salt and water.

As reference sample $GeCl_4$, which is a neat liquid, was used. This compound was from Schuchardt GmbH, München; it has a purity of 99,999%.

The measuring temperature of all samples was (305 ± 1) K.

3. Results

3.1 The Ratio of the Larmor frequencies of ^{107}Ag and ^{109}Ag

To determine this ratio, the following four samples were used:

No. 1: Aqueous solution 9.63 molal in $AgNO_3$,
No. 2: Aqueous solution 2.51 molal in $AgClO_4$,
No. 3: Aqueous solution 8.3 molal in AgF,
No. 4: Aqueous solution 9.08 molal in $AgNO_3$ and 0.24 molal in $Fe(NO_3)_3$.

Altogether 82 ratios of the Larmor frequencies of the silver isotopes were measured, the result is

$$\nu(^{109}\mathrm{Ag})/\nu(^{107}\mathrm{Ag}) = 1.149\,639\,7\ (8)\ .$$

This relative error of 0.7 ppm is three times the r.m.s. error. The results obtained from the four samples are all within these limits of error given here, i. e. a primary isotopic effect was not to be detected, so it is surely less than 0.7 ppm.

This ratio of the Larmor frequencies of ^{107}Ag and ^{109}Ag has to be compared with former results: It is in agreement with the value

$$\nu(^{109}\mathrm{Ag})/\nu(^{107}\mathrm{Ag}) = 1.149\,624\ (38)$$

calculated from the results of Brun et al. [2], but it is slightly outside the limits of error of the value of Sogo and Jeffries [3]:

$$\nu(^{109}\mathrm{Ag})/\nu(^{107}\mathrm{Ag}) = 1.149\,62\ (1)\ .$$

3.2 *Hyperfine Structure Anomaly*

The hyperfine structure anomaly of two isotopes 1 and 2 is defined by

$$^1\Delta^2 = \frac{A_1/A_2}{g_{I_1}/g_{I_2}} - 1\ .$$

A_1 and A_2 are the hyperfine interaction constants of the atomic state in question, whereas g_{I_1} and g_{I_2} are the nuclear g-factors. In the $^2\mathrm{S}_{1/2}$ ground state of the Ag atom, Dahmen and Penselin [11] have determined the hyperfine structure separation of both isotopes ^{107}Ag and ^{109}Ag with high accuracy using the atomic beam magnetic resonance technique:

$$\Delta\nu(^{107}\mathrm{Ag}) = 1712.512\,111\ (18)\ \mathrm{MHz}$$
$$\text{and}\quad \Delta\nu(^{109}\mathrm{Ag}) = 1976.932\,075\ (17)\ \mathrm{MHz}\,.$$

These results together with the ratio of the Larmor frequencies from the present work, yield for the hyperfine structure anomaly of the Ag isotopes in the atomic ground state:

$$^{107}\Delta^{109} = \{\Delta\nu(^{107}\mathrm{Ag})\cdot\nu(^{109}\mathrm{Ag})\}/\{\Delta\nu(^{109}\mathrm{Ag})\cdot\nu(^{107}\mathrm{Ag})\} - 1 = -0.004\,127\,7\ (7)\ .$$

The error of this result, is due to the uncertainty of the ratio of the Larmor frequencies of ± 0.7 ppm as given above. This hyperfine structure anomaly is in agreement with the result of Sogo and Jeffries [3]:

$$^{107}\Delta^{109} = -0.004\,12\ (6)\ .$$

3.3 *Relaxation Times*

Comparing the intensities of the ^{107}Ag and ^{109}Ag NMR signals with those of nuclei with similar gyromagnetic ratios, e. g. ^{87}Sr [12], the signal intensities of the Ag isotopes in AgNO$_3$ solutions are weaker than expected about by factor 3. The only reason for this may be an unfavourable ratio T_1/T_2, as the intensity of the NMR signal recorded with the Quadriga technique is [13] $\sim \sqrt{T_2/T_1}$.

This ratio was determined for the ^{107}Ag and the ^{109}Ag resonances in a 9.1 molal aqueous solution of AgNO$_3$: $T_1/T_2 \approx 12$. By paramagnetic admixtures this ratio can be reduced: for samples with 0.24 molal and 0.93 molal Fe(NO$_3$)$_3$ concentrations the ratios were $T_1/T_2 \approx 4$ and $T_1/T_2 \approx 2$ respectively. For the ^{109}Ag resonance in 8.3 molal aqueous solution of AgF there is the ratio $T_1/T_2 = 6 \pm 1$ and the relaxation times are $T_1 = (49 \pm 20)$ sec and $T_2 = (8.2 \pm 2)$ sec. The resonances of other nuclei with $\mathrm{I} = 1/2$ and small magnetic moments, e. g. ^{111}Cd, ^{113}Cd [14], ^{115}Sn, ^{117}Sn, and ^{119}Sn [15], show similar ratios T_1/T_2 in aqueous solutions.

A detailed and systematical determination of the silver relaxation times of Ag$^+$ ions as well as of Ag complexes is in progress.

To reduce the measuring time, it is worth while using a silver sample with paramagnetic ions, as reference for all shift measurements.

3.4 *Shift of the ^{107}Ag Larmor frequency due to Paramagnetic Ions*

All former NMR measurements of ^{107}Ag and ^{109}Ag [2, 3] were performed with aqueous solutions of AgNO$_3$ containing paramagnetic ions. To determine the shift resulting from such admixtures, and on the other hand to find the optimum reference sample for shift measurements, the influence of paramagnetic Fe(NO$_3$)$_3$ admixtures to the sample (aqueous AgNO$_3$ solution) on the ^{107}Ag Larmor frequency was determined systematically. The AgNO$_3$ concentration of all samples was 9.1 molal, whereas the Fe(NO$_3$)$_3$ concentration was varied in the range of 0 . . . 1.2 molal. The measurements were carried out with spherical samples of 21 mm internal diameter, in order that no corrections for bulk susceptibility are necessary. The result is given in Figure 2; the errors are three times the r.m.s. errors resulting from about 10 measurements with each sample, performed alternately with the reference sample.

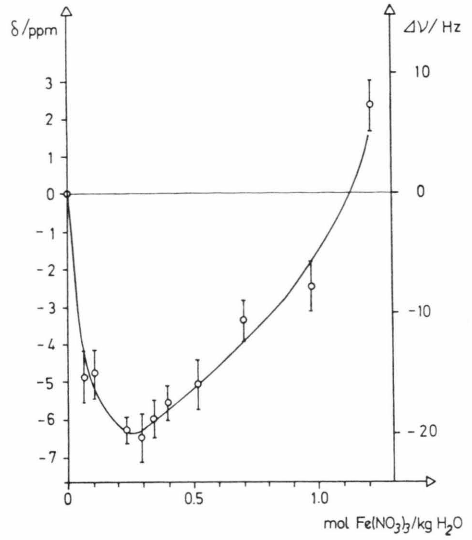

Fig. 2. Shift of the ^{107}Ag NMR line by paramagnetic $Fe(NO_3)_3$ admixtures. All samples are aqueous solutions 9.1 molal in $AgNO_3$. The right ordinate scale gives the absolute shift $\Delta\nu = \nu_0 - \nu_x$, where the resonance frequency of an $AgNO_3$ solution without $Fe(NO_3)_3$ is $\nu_0 = 3.114$ MHz; the left scale shows the relative shift $\delta = (\nu_0 - \nu_x)/\nu_0$ in ppm.

The maximum shift in the range of $Fe(NO_3)_3$ concentrations, investigated here, is 26 Hz or 8.3 ppm. The shift of the ^{107}Ag resonance is no monotonous function of the concentration of paramagnetic ions. In the range 0.2 . . . 0.3 molal $Fe(NO_3)_3$ concentration, the shift is extreme $\delta = (-6.4 \pm 0.6)$ ppm and changes only slightly with the concentration. This trend of the shift is not to be explained by the theories of Bloembergen [16] and Swift et al. [17], which do not describe the change of the sign of the derivative of the function: shift against concentration of paramagnetic ions. Perhaps the change of sign may be explained by the formation of a short lived complex at higher $Fe(NO_3)_3$ concentrations.

3.5 The Ratio of the Larmor frequencies of ^{107}Ag and ^{73}Ge, and also of ^{109}Ag and ^{73}Ge

Two well defined silver samples were used as reference for all chemical shift measurements: samples No. 3 and No. 4 mentioned in Section 3.1. Beside the highest possible concentration of Ag^+ ions, the ratio of the relaxation times T_1/T_2 should be as low as possible. Sample No. 4 contains a 0.24 molal admixture of paramagnetic $Fe(NO_3)_3$; this concentration was chosen, as the Larmor frequency is nearly independent of the concentration of the Fe^{3+} ions in this range (see Section 3.4), and on the other hand this admixture reduces the measuring time for the reference by factor 3.

For these two samples the frequency ratios $\nu(^{107}Ag)/\nu(^{73}Ge)$ and $\nu(^{109}Ag)/\nu(^{73}Ge)$ were determined. The ^{73}Ge resonance in $GeCl_4$ is a well defined standard as this Larmor frequency is referred to that of ^{2}H with high accuracy [18].

The halfwidth of the NMR lines of the Ag isotopes as well as of ^{73}Ge was about 30 Hz, which is due to the Quadriga technique. Silver sample and reference sample were measured alternately in the same probe assembly, which was tuned for the new frequency before each measurement. For the cylindrical AgF sample, and also for the spherical $AgNO_3$ sample the total measuring time was 12 minutes (4 × 3 min). The measurements were performed on 6 different days. The results are given in Table 1.

All frequency ratios measured with cylindrical samples, were corrected for bulk susceptibility to spherical shape, using the susceptibilities $\chi(GeCl_4) = -0.63 \cdot 10^{-6}$ (see [19]) and χ(sample No. 4) $= -0.98 \cdot 10^{-6}$ calculated from the molar susceptibility of AgF $\chi_{mol} = -38.4 \cdot 10^{-6}$ cm^3/mol [20]. The errors given in Table 1 are three times the r.m.s. errors.

Table 1. Ratios of the Larmor frequencies of ^{107}Ag, ^{109}Ag and ^{73}Ge. The ratios measured with cylinders are corrected for bulk susceptibility to spherical shape of the sample.

Sample No.	Solution	Shape of the Sample	No. of Ratios Measured	$\nu(^{107}Ag)/\nu(^{73}Ge)$	$\nu(^{109}Ag)/\nu(^{73}Ge)$
3	Aqueous solution 8.3 molal in AgF	Cylinder 21 mm internal diam.	24	1.160 397 2 (7)	1.334 039 2 (7)
4	Aqueous solution 9.08 molal in $AgNO_3$ and 0.24 molal in $Fe(NO_3)_3$	Sphere 17 mm internal diam.	36	1.160 325 6 (4)	1.333 957 0 (5)

3.6 Concentration Dependence

For aqueous solutions of the salts $AgNO_3$, $AgClO_4$, and AgF, the dependence of the Larmor frequencies on the concentration in the range 0.4 molal up to nearly saturated solutions, was determined. For each sample about 15 measurements were taken alternately with one of the reference samples described in Section 3.5. To reach a great filling factor, which is particularly necessary for low concentrations, all samples were measured in cylinders. In Fig. 3 the results are given: the shifts are plotted against the concentrations of the samples. The ordinate scale is adjusted so that all shifts refer to the Larmor frequency ν_0 of the Ag$^+$ ion at infinite dilution as standard. This frequency may be obtained by extrapolation of all three curves to zero concentration.

The ^{107}Ag resonance was investigated to get the shifts of the $AgNO_3$ and the $AgClO_4$ solutions, whereas in the AgF solution the ^{109}Ag resonance was observed.

Cylindrical samples were used, all measured frequencies were corrected for bulk susceptibility to spherical shape. For the diamagnetic samples these corrections are small and can be calculated; but the correction for the paramagnetic reference sample No. 4 (See Sect. 3.1) had to be determined experimentally: the ratio of the Larmor frequencies $\nu(^{107}\mathrm{Ag})/\nu(^{73}\mathrm{Ge})$ was measured with cylindrical samples, this ratio is less than the ratio measured with spheres by 2.32 ppm, together with the well known susceptibility of $GeCl_4$ this yields the result that the silver Larmor frequencies of sample No. 4 measured with spheres are greater than those measured with cylinders, by 1.0 ppm.

The errors given in Fig. 3 are three times the r.m.s. errors. The uncertainty of the extrapolation to zero concentration, i. e. the uncertainty of the adjustment of the ordinate scale, may be assumed ±1 ppm. The shifts of the two reference samples are now:

$$\delta\ (\text{Ref. No. 3}) = (-14.0 \pm 1)\ \text{ppm}$$
$$\text{and}\quad \delta\ (\text{Ref. No. 4}) = (+47.3 \pm 1)\ \text{ppm}\,.$$

3.7 Ratios of the Larmor frequencies for Infinite Dilution and the Nuclear Magnetic Moments of ^{107}Ag and ^{109}Ag

Using the shifts of the two reference samples No. 3 and No. 4 relative to the Larmor frequency of the Ag$^+$ ion surrounded only by water molecules, as given in Sect. 3.6, together with the results of Table 1, there are the ratios of the Larmor frequencies for infinite dilution of the Ag salts:

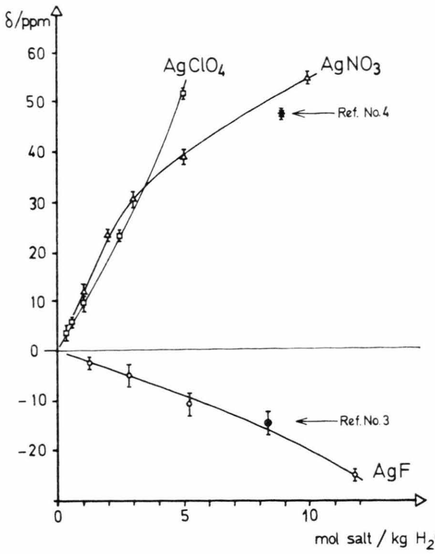

Fig. 3. ^{107}Ag and ^{109}Ag chemical shifts in aqueous solutions of silver salts as a function of the concentration. The shifts plotted on the ordinate are defined $\delta = (\nu_0 - \nu_x)/\nu_0$, where ν_0 is the Larmor frequency of the Ag$^+$ ions at infinite dilution. The two reference samples No. 3 and No. 4 are marked; the result of reference No. 4 is not situated on the $AgNO_3$ curve as it contains paramagnetic $Fe(NO_3)_3$.

$$\{\nu(^{107}\mathrm{Ag}^+)/\nu(^{73}\mathrm{Ge})\}_{\text{extrapol.}} = 1.160\,380\,7\ (15)$$

and

$$\{\nu(^{109}\mathrm{Ag}^+)/\nu(^{73}\mathrm{Ge})\}_{\text{extrapol.}} = 1.334\,020\,3\ (17)\,.$$

With the ratio $\nu(^{73}\mathrm{Ge})/\nu(^{2}\mathrm{H})$ in $GeCl_4$ and D_2O [18] and the ratio $\nu(^{2}\mathrm{H})/\nu(^{1}\mathrm{H})$ in D_2O and H_2O [21] the Larmor frequencies of the silver ions are referred to those of ^{2}H in D_2O and ^{1}H in H_2O.

With the magnetic moment of the proton in H_2O (uncorrected for diamagnetism) of Taylor et al. [22] and the sign of the silver magnetic moments by Jackson and Kuhn [1] the magnetic moments of the silver isotopes may be calculated. These moments are affected with the uncertainty of the magnetic moment of the proton and they are not corrected for the ionic diamagnetism. The results are given in Table 2.

The frequency ratios of Table 2 have to be compared with former results: Brun et al. [2] have determined the ratios

$$\nu(^{107}\mathrm{Ag})/\nu(^{1}\mathrm{H}) = 0.040\,468\ (1)$$
$$\text{and}\quad \nu(^{109}\mathrm{Ag})/\nu(^{1}\mathrm{H}) = 0.046\,523\,(1)$$

Result	^{107}Ag	^{109}Ag
$\{\nu(\mathrm{Ag}^+)/\nu(^2\mathrm{H})\}_{\mathrm{extrapol.}}$	0.263 694 7 (12)	0.303 154 0 (14)
$\{\nu(\mathrm{Ag}^+)/\nu(^1\mathrm{H})\}_{\mathrm{extrapol.}}$	0.040 478 74 (18)	0.046 535 98 (22)
$\mu(\mathrm{Ag}^+ \text{ in } \mathrm{H_2O})/\mu_\mathrm{N}$	−0.113 045 3 (9)	−0.129 961 5 (10)

Table 2. Ratios of the Larmor frequencies of silver ions in water, relative to those of ^{2}H in D_2O and ^{1}H in H_2O, and the nuclear magnetic moments of Ag$^+$ merely surrounded by water molecules, not corrected for ionic diamagnetism.

using as sample an aqueous solution 7 molar in $AgNO_3$ and 1.0 molar in $Mn(NO_3)_2$. The differences between the results of Table 2, and the values of Brun et al. are about 270 ppm, this is more than 10 times the uncertainty given by these authors. This discrepancy can not be explained by paramagnetic admixtures, as is to be seen from Fig. 2. The result of Sogo and Jeffries[3]

$$\nu(^{109}\mathrm{Ag})/\nu(^2\mathrm{H}) = 0.303\,16(3)$$

is in agreement with the ratio in Table 2.

3.8 *The Shielding Constant of Ag$^+$ Ions in Water*

Performing a NMR experiment, in a solution in a static magnetic field B_0 there is the Larmor frequency

$$\omega_\mathrm{L} = 2\,\pi\,\nu_\mathrm{L} = (\mu_\mathrm{NMR}/I\,\hbar)\,B_0 = (\mu_\mathrm{nucleus}/I\,\hbar)\,B = \gamma_\mathrm{NMR}\,B_0 = \gamma\,B\,.$$

There is μ_NMR the magnetic moment as measured in a NMR experiment, e. g. for the silver isotopes these moments are given in Table 2; whereas μ_nucleus is the magnetic moment of a bare nucleus without any shielding by the electrons. The gyromagnetic ratios γ_NMR and γ are defined in the same manner. B is the field at the position of the nucleus shielded by the electrons of the atom or ion, and also by surrounding molecules, it is

$$B = (1-\sigma)\,B_0\,.$$

There is the shielding constant:

$$\sigma = 1 - B/B_0 = 1 - \mu_\mathrm{NMR}/\mu_\mathrm{nucleus} = 1 - \gamma_\mathrm{NMR}/\gamma\,.$$

For the silver isotopes there is no experimental determination of μ_nucleus, however the nuclear magnetic moment of ^{107}Ag in the silver atom was measured with the atomic beam magnetic resonance technique by Penselin, Schumacher, and Wolber[23]

$$\mu(^{107}\mathrm{Ag\ atom}) = -0.112\,939\,(20)\,\mu_\mathrm{N}\,.$$

This value and our result of Table 2 yield a shielding constant

$$\sigma^*\ (\mathrm{Ag}^+ \text{ in } \mathrm{H_2O} \text{ vs. Ag atom}) = 1 - \frac{\mu\ (\mathrm{Ag}^+ \text{ in } \mathrm{H_2O})}{\mu\ (\text{atomic beam})} = -0.000\,94\,(17)$$

for both silver isotopes, as there is no primary isotopic effect. This constant describes the shielding of the magnetic field B_0, by the water molecules and ions surrounding the Ag$^+$ ion under investigation, except for the small difference in the shielding of the silver nucleus by the electrons of the atom and the ion, which is below the uncertainty given here[24, 25].

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